Passivation and activation of $La_{0.6}Sr_{0.4}FeO_3$ thin

film electrodes

- Supporting Information -

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1. Testing setup



Figure S1. a) Thin film electrode after PLD (only around 2/3 of the electrolyte area is covered due to a physical mask used during PLD); b) Experimental setup for electrochemical impedance spectroscopy (EIS). Most parts are alumina. The gold meshes (wrapped around CGO pellets) can be seen on all three sample holders; c) Four probe setup for electrical conductivity relaxation (ECR) of thin films

2. XRD of as deposited electrode

XRD diffractogram of the as deposited thin film electrode is shown in Figure S2. The observed peaks originate from (100)-oriented YSZ substrate and only specific crystallographic planes of the CGO buffer layer and LSF thin film. This is a strong indication of thin film texture due to preferential growth along (100) direction. The lattice parameters of YSZ and CGO are 5.12 and 5.42 Å, respectively which gives a lattice mismatch of approximately 6%. In our prior work, *a* and *b* unit cell parameters of bulk LSF were found to be 5.53 Å¹, which is 2 % larger than CGO. The deposited thin films are thus expected to be under the compressive strain. Since both YSZ and CGO belong to the cubic *Fm-3m* space group (Figure S2c, d) and due to a small lattice mismatch, the 'cube on cube' epitaxial growth can be expected in case of CGO film². On the other hand, LSF (La_{0.6}Sr_{0.4}FeO₃) in bulk belongs to the rhombohedral *R-3ch* space group (Figure S2b) at the experimental conditions used in this study. This space group is characterized by angle of 120°C between x and y axis. Therefore, instead of direct 'cube on cube', LSF is expected to grow with an offset of $\frac{1}{2}$ of the unit cell.



Figure S2. XRD diffractogram of the as deposited LSF thin film (a). Unit cells of LSF (b), CGO (c) and YSZ (d), projected along the z-axis.

3. SEM and film thickness

Figure S3 illustrates schematically the produced cells and SEM images of the surface and cross-sections of the working electrode (LSF + CGO buffer layer) and counter electrode (Pt infiltrated with CPO) before the test. The cross section is obtained by cracking the sample (Figure S3b). The two deposited layers are clearly distinguishable. The thicknesses of the CGO and the LSF layers determined from cross-sections of three cracked samples are 35 ± 5 and 215 ± 5 nm, respectively. Similar results are obtained by thickness measurement with a Dektak stylus profiler (≈ 260 nm, Figure S3d). The obtained surface profile indicates that CGO buffer layer is buried in LSF (Figure S3e). The microstructure of the electrodes could not be clearly resolved, but the films appeared fully dense and flat. The surface of the deposited LSF film is uniform with no observable cracks or extended facets (Figure S3c). The image on the bottom shows the microstructure of the counter electrode is approximately 15 µm. A CPO layer is visible around the Pt backbone.



Figure S3. A sketch illustrating the half-cell consisting of thin LSF film with CGO buffer layer as working electrode, YSZ electrolyte, and CPO-infiltrated platinum serving as counter electrode. Adjacent are SEM images of the cross section of counter electrode (a) and working electrodes (b) and LSF surface before the electrochemical testing (c). Plot on the right shows thickness measurement by a Dektak stylus profiler (d), as well as a sketch to help interpret Dektak measurements (e).

4. Interpretation of impedance spectra

Electrochemical impedance spectroscopy enables the determination of many parameters relevant to the electrochemical performance of materials. A typical impedance spectrum obtained in this study is shown in Figure S4.



Figure S4. Nyquist plot of a typical impedance spectrum obtained in this study.

The impedance response is measured from high to low frequency in the range from 100 kHz to 0.1 Hz. There are three distinguishable features in the illustrated spectrum: a semicircle at low-frequencies (red), a depressed semicircle at mid-frequencies (green), and serial resistance at high frequencies (spectrum intercept with Z_{real} -axis). The simplest equivalent circuit that is able to fit the experimental data is an R(RQ)(RC) circuit consisting of a resistor connected in series with a RQ and RC circuits. Here R stands for a resistor, Q for a constant phase element (CPE), and C for a capacitor. The equivalent circuit is mathematically equivalent to the R(Q(R(RC))) circuit used by Baumann et al.³, and therefore the spectra could equally well be fitted with the latter. The only difference between the two circuits is the physical interpretation of the CPE. Parametrization and the physical interpretation of the observed spectrum features are discussed below.

Low frequency part

At low frequency, the spectrum can be simulated with a semicircle in a Nyquist plot (RC circuit). This is part of spectrum is commonly associated with surface resistance due to oxygen exchange reaction (R_{ORR}) connected in parallel with a capacitor. The capacitive part is usually associated with chemical capacitance (C_{chem}) related to oxygen stoichiometry changes in the bulk of the electrode^{3,4}. Boukamp *et al.* have derived a general impedance model for dense MIEC electrodes under the assumptions of good electronic conductivity and small perturbations of electrical potential and obtained the following relations between R_{ORR} and C_{chem} and oxygen transport parameters; surface exchange coefficient (k_{chem}) and chemical diffusion coefficient (D_{chem})⁵:

$$R_{ORR} = Z_0 \left[\frac{1}{k_{chem}} + \frac{L}{D_{chem}} \right] \qquad (SE1)$$
$$C_{chem} = \frac{1}{Z_0 \left[\frac{1}{L} + \frac{k_{chem}}{D_{chem}} \right]} \qquad (SE2)$$

Where

$$Z_0 = \frac{RT}{n^2 F^2 A C_0} \cdot \gamma = \frac{RT}{8F^2 A C_0} \cdot \frac{\partial \ln p O_2}{\partial \ln C_0} \approx -\frac{RT V_M}{8F^2 A} \frac{\partial \ln p O_2}{\partial \delta}$$
(SE3)

Here, *R* is the universal gas constant, *T* is temperature, *n* is the charge of the diffusing ion (-2 for oxygen), *F* is Faraday's constant, *A* is the surface area of the electrode, C_0 is the concentration of oxygen ions in the lattice, a_0 and pO_2 stand for activity and partial pressure of oxygen, V_M is the molar volume of the oxide, and γ is thermodynamic enhancement factor defined as:

$$\gamma = \frac{1}{2} \frac{\partial \ln(pO_2)}{\partial \ln(C_0)} \qquad (SE4)$$

Due to specific geometry of thin films and good ionic conductivity of LSF we can assume that after being incorporated at the electrodes surface, oxygen ions diffuse through the volume of the electrode instantaneously. When $D_{chem} \rightarrow \infty$ the equations SE2 and SE3 simplify to:

$$R_{ORR} = \frac{RT}{n^2 F^2 A C_0} \cdot \gamma \cdot \frac{1}{k_{chem}} = \frac{RT}{n^2 F^2 A C_0} \cdot \frac{1}{k_0} \qquad (SE5)$$
$$C_{chem} = \frac{n^2 F^2 A L C_0}{RT} \cdot \frac{1}{\gamma} \approx -\frac{8F^2}{RT V_M} \frac{\partial \delta}{\partial \ln p O_2} \qquad (SE6)$$

Equation SE5 is usually used in the literature for the calculation of k_0 from area specific resistance $(ASR = R_{ORR}A)^{3,6}$.

The impedance spectrum of thin MIEC electrode can provide even more information. It is well known that the time constant of an RC circuit can be written as:

$$\tau_{RC} = \frac{1}{2\pi f_{summit}} = R \cdot C \qquad (SE7)$$

Where f_{summit} is the frequency corresponding to the summit (maximum Z_{imag}) of the impedance arc. Therefore, by combining the equations SE1, SE2, and SE7 we can express the time constant of oxygen exchange in terms of R_{ORR} and C_{chem} :

$$\tau_{ORR} = R_{ORR} \cdot C_{chem} = \frac{L}{k_{chem}} \qquad (SE8)$$

Equation SE8 enables the determination of k_{chem} from a dense MIEC electrode of known thickness when the electrode is in a surface-controlled regime (i.e when diffusion through the thin film can be neglected). Furthermore, based on the known relation between k_0 and k_{chem} :

$$\gamma = \frac{k_{chem}}{k_0} \qquad (SE9)$$

we can use the calculated k_0 and k_{chem} values for estimation of thermodynamic enhancement factor, γ .

Medium frequency part

The depressed semicircle found in the mid-frequency range is simulated by a RQ circuit consisting of a resistor and a constant phase element (CPE) connected in parallel. The exponent of the constant phase element had values in range 0.7-0.85. Similar observations have been reported in many MIEC thin film electrodes. Baumann et al.³ attributed this feature to the interfacial resistance and capacitance between electrode and the electrolyte. The resistive element is associated with the transfer of oxide ions between electrode and electrolyte.³ Pseudocapacitance of the CPE element (C_{MF}) is calculated using the following formula:

$$C_{MF} = (R_{MF}^{1-n}Q_{MF})^{1/n} \qquad (SE10)$$

The calculated values were typically 4-8 times smaller than the capacitance associated with LSF layer (C_{chem}). Since chemical capacitance is an extensive quantity, this might be an indication that the C_{MF} is associated with the CGO buffer layer which is approximately 6 times thinner than LSF electrode.

High frequency part

At high frequencies, the imaginary part of impedance response approaches zero and the spectrum consists of series resistance only. This characteristic is also found to be independent of pO_2 and is therefore attributed to the resistance of the electrolyte (R_{YSZ}). In a study by Baumann et al.⁶, based on ~300 measurements the authors have obtained an empirical relation for the ionic conductivity of 9.5 mol % Y₂O₃-doped ZrO₂ (the same material and supplier as in this study):

$$\sigma_{YSZ} = 1000 \pm 100 \exp\left(-\frac{0.93 \pm 0.02 \ eV}{kT}\right) \frac{S}{cm}$$
 (SE11)

Based on this equation we have estimated the resistance of a 0.5 cm thick ($L_{YSZ} = 0.5 cm$) YSZ electrolyte with an area of $A_{YSZ} = 1 cm^2$ using the following relation:

$$R_{YSZ} = \frac{1}{\sigma_{YSZ}} \cdot \frac{L_{YSZ}}{A_{YSZ}} \qquad (SE12)$$

In order to check whether the YSZ substrates we received had the same resistance, we measured the series resistance values obtained from a symmetrical cell made of 10 μ m thick and screenprinted LSCF/CGO electrodes (LSCF stands for La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O₃). The symmetrical cells with thick and well conductive layers are used in order to ensure that the whole electrolyte volume is active and avoid possible problems with sheet resistance. It can be seen that resistance values obtained in this way match very well with the values calculated using the empirical equation by Baumann *et al.* (Figure S5).



Figure S5. A comparison of the resistance values obtained from YSZ conductivity test in a symmetrical cell setup (R_{YSZ}) with two well performing composite electrodes and serial resistance associated with YSZ electrolyte obtained from thin film electrode test (R_{series}). The values calculated from the empirical equation given by Baumann et al.⁶ are shown as well.

However, the values of the series resistance obtained from the half-cells with the thin film working electrode and Pt+CPO counter electrodes were systematically higher, while the apparent activation energy was similar and close to 0.9 eV. The observed high values can be a consequence of a reduced active area (volume) of the electrolyte. This may be a consequence of (a) partial contact at the working electrode due to misalignment, (b) lack of mechanical contact between the auxiliary gold mesh and the working electrode, (c) "long" distance between contact points at the working electrode (on the length-scale of the working electrode thickness) which may result in a significant contribution of sheet resistance (Figure S6).



Figure S6. Possible reasons for reduced active area of the electrolyte and the schematic description of YSZ conductivity measurement by a LSCF/CGO||YSZ||LSCF/CGO symmetrical cell

The first two types of imperfections are the result of the particular experimental setup with sandwiched cells. The cell can be misaligned with regards to the current collectors. This renders parts of the electrode and the electrolyte inactive. The second problem arises when such setup is used for testing of thin film electrodes. Current collectors consisting of woven gold (prone to deformation by creep) might not establish the perfect contact with the flat thin film surface. Further, some parts of electrode and the underlying electrolyte can be inactive due to sheet resistance.^{7,8} This effect is aggravated in case of thinner electrodes, faster surface reaction, and low electrical conductance of the working electrode (either due to cracks/porosities or low material conductivity). Even in the case of perfect contacting with LSF electrode ($A_{act.} = A_{LSF}$), the active volume of electrolyte will be reduced since the films are deposited only on approximately 2/3 of the electrolyte cross section ($A_{YSZ} = 1 \text{ cm}^2$)⁹. In the case of the symmetrical cell, thick and well conducting layers ensure that current is spread all across the electrolyte surface even if the contacting of mesh to electrode is not perfect. Following this line of argumentation we can use the difference in measured series resistance for estimation of the active area for the working electrode and subsequent normalization of the impedance response:

$$A_{act.} \cdot R_{serial} = A_{YSZ} \cdot R_{YSZ} \rightarrow A_{act.} = \frac{R_{YSZ}}{R_{serial}} (cm^2)$$
 (SE13)

Figure S7 illustrates the differences between electrolyte area (A_{YSZ}), electrode area (A_{LSF}), and active area (A_{act.}) calculated using the equation SE13. Estimation of the active area of non-modified LSF electrode shows that approximately $\frac{1}{2}$ of the total electrode area is active. Interestingly, the apparent active area appears to pass through a maximum at \approx 425°C and seems to decrease with the increasing temperature which resembles temperature dependence of LSF conductivity.¹ This may indicate that higher electrical conductivity at lower temperatures can partially compensate for some of the flaws presented in Figure S6.

It should be noted that this "effective area correction" is not an accurate account of the effects of imperfect contact at the working electrode on the deduced polarization resistance (or k values) but the "corrected" values are likely closer to the real ones than if these effects are neglected. In other words; corrected values may be considered a lower bound whereas the uncorrected values for sure represent an upper bound.



Figure S7. Estimation of the active electrode area (A_{act}) calculated as R_{serial}/R_{YSZ} and comparison with electrolyte area (A_{YSZ}) and electrode area (A_{LSF})

5. Chemical capacitance

The results of temperature-dependence and pO₂-dependence of chemical capacitance are shown in Figure S8. The apparent chemical capacitance are normalized to the active volume (A_{act}·L). The obtained values were between 1000 and 1150 F/cm³ and similar to values reported previously in the literature for perovskite thin films.^{6,10} It can be seen that chemical capacitance is only mildly dependent on temperature in the experimental range of this study. Since chemical capacitance is related to changes in electrode stoichiometry (formation of oxygen vacancies)^{3,4,11}, relative insensitivity to temperature of C_{chem} can be explained in terms of the very small defect concentration changes in La_{0.6}Sr_{0.4}FeO₃ below 600°C in the investigated pO₂ range.¹² The pseudocapacitance measured at 491°C shows an increase with decreasing pO₂ (see Fig. S8). The slope of linear fit through the measurement points was found to be 7.85 $\cdot 10^{-3}$. The increase in C_{chem} with the decreasing pO₂ reflects the formation of an increased amount of oxygen vacancies.



Figure S8. Left) chemical capacitance of the low frequency semicircle (C_{chem}) and pseudocapacitance of the constant phase element (Q_{MF}) at different temperatures in oxygen; Right) pO₂-dependence of C_{chem} at 491°C.

6. Calculation of thermodynamic enhancement factor

Based on the calculated k_{chem} and k_0 values, the thermodynamic enhancement factor is calculated using Eq. SE9. The values varied from 45-95 over the tested temperature range, while at different pO₂ at 491°C γ remained constant and close to ≈ 80 .



Figure S9. Thermodynamic enhancement factor (γ) at (left) different temperatures and pO₂ = 1 bar; (right) different pO₂ and T = 491°C.

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